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Program Monitor John Prater
7/1/02 – 6/30/05

1. **Forward** – Not Submitted
2. **Table of Contents** – Not Required
3. **List of Appendixes, Illustrations and Tables** – None
4. **Statement of Problem Studied**

This program focused on the synthesis of nanoparticles of metals and semiconductors, their properties, and the processes underlying their growth. We used a growth technique that we developed, namely buffer-layer-assisted growth (BLAG), and characterized the particles with transmission electron microscopy. We also used photoluminescence to study the Ge quantum dots. In BLAG, we condense a noninteractive buffer layer like Xe on a surface of choice at low temperature (any surface would do), and then use physical vapor deposition to deliver atoms of a second material of choice to the buffer. Those atoms are mobile, even at ~20 K, and they form small clusters. Subsequent warm-up and desorption of the buffer activates diffusion and aggregation so that the density and size of the nanoparticles that ultimately reach the substrate can be controlled.

Under this program, we focused on understanding the mechanism underlying diffusion, how the particles aggregated, whether aggregation gave rise to compact or branched (ramified) structures and how the various parameters could be tuned to produce the desired sizes and distribution. We used TEM as the primary technique for quantifying the dependence of density and size on buffer layer thickness, warm-up rate, make up of the buffer (Xe, Ar, Kr), and the cluster material (Cu, Ag, Au, Co, Ni, Pd, Ge). The ultimate applications of this program would be in photonics (Ge, CdSe and other quantum dots), novel magnetics (device structures based on nanoscale magnets), and the understanding of material issues at the nanoscale.

5. **Summary of Most Important Results**

Where this work fits in the broader context is that major efforts worldwide are currently devoted to producing and utilizing nanoscale materials. The challenge is in the synthesis of those materials, first, and then the incorporation of them into larger structures that would be useful. Incorporation raises critical issues related to stability and the properties of the interfaces that are formed. They are particularly important for particles derived from finite numbers of atoms. Our approach is the bottom-up approach with self-assembly from constituent atoms and molecules. In general, that approach is severely limited because of constraints related to thermodynamics that restrict the growth of three-dimensional nanoparticles to a small number of elements and surfaces. What we have done with buffer-layer-assisted growth is circumvent those constraints.

We introduce a buffer that can be formed on any substrate and then removed simply by warming to room temperature. Since the buffer is inert, it introduces no chemistry. Clusters form on the buffer, and three-dimensional nanoparticles of (almost) anything can be synthesized. Our work is unique in that it allows us to deliver to a surface of choice, clusters that range in size from tens to tens of millions of atoms under controlled, pristine conditions and study their interactions. This greatly expands the parameter space of nanoscale dry synthesis, and we are interested in issues that involve the interfaces formed when the nanoparticles come in contact with the no-longer-

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Enclosure 1

buffered substrate, the degree of wetting, the kinetic stabilization of the particles, and the properties of zero and one-dimensional quantum confined structures.

The main findings include:

- 1) We were able to demonstrate that the technique of BLAG is widely applicable to synthesize both metal and semiconductor nanoparticles. We have also been able to extend the synthesis to ionic compounds producing novel structures whose rates of growth, shapes, and sizes depend on the dipolar interaction between the material and the buffer.
- 2) We were able to quantitatively model the dependence of particle density and sizes on buffer layer thickness, thus making it possible to design cluster density/size patterns.
- 3) Comparison between simulations and particle shapes indicated that the reduction in particle density was due to diffusion-limited cluster-cluster aggregation.
- 4) We showed that aggregation could be influenced by a molecular coating on the particles, using a CO monolayer to coat Pd particles. The primary effect of the coating was to reduce coalescence, giving rise to more ramified structures for the same amount of Pd.
- 5) Detailed studies of Au nanoparticle formation on the highly-incommensurate surfaces of solid Xe, Kr, and Ar demonstrated that the diffusivity varied strongly with particle size for small particles but then converged to a value that reflected fast slip diffusion. Significantly, the motion was driven by the phonons of the substrate and was controlled by friction between a cluster facet and the buffer (the contact area)
- 6) Studies of the effect of buffer thickness and the rate of desorption on the aggregation of metal particles allowed us to determine the activation energies and the prefactors for diffusion for these novel, atomically-clean structures. We found that the barriers were small, consistent with the incommensurate interface, and, surprisingly, the prefactors scaled with the barriers to compensate as the barrier increased due to the Meyer-Neldel effect. Analysis made it possible to demonstrate that the energy of diffusion is related to the phonons of the buffer. We proposed that this phonon-activated behavior should be a general characteristic of nanoparticle diffusion.
- 7) Amorphous-Ge nano-particles grown by BLAG exhibit a broad luminescence peak centered at 0.91 eV, expected to be due to recombination between the conduction and valence band tails of localized states. The peak did not shift with particle size or temperature in the range of 3 - 150 K as confinement effects were suppressed by the very high density of dangling-bond-type defects in the amorphous phase. The defect density was estimated to be $\sim 10^{20} \text{ cm}^{-3}$ from optical absorption measurements. The rate of decay of the PL signal as a function of temperature indicated a carrier diffusion length of less than 10 Å.
- 8) As the program was coming to an end, we sought to demonstrate that the concepts and procedures of BLAG with rare gas buffers could be extended to buffers of more complex molecular solids, including solid CO and H₂O (ice). Those buffers would extend BLAG as a growth pathway for nanoparticles to higher temperature. We also sought to demonstrate that nanostructures could be formed for materials that were more complex than elementary solids, including CdSe (for photonic applications), CsI grown on H₂O (ice) (as a representative salt), and LaF₃ (as a bulky molecule where diffusion would be constrained).

Direct contacts with Army, DOD, and industrial personnel – None.

6. List of papers submitted or published

(a) published in peer reviewed journals

K.S. Nakayama and J.H. Weaver, "Ag Multilayer Island Growth on Br-Si(001)-(2x1) and Ag-induced Nano-pitting," Surf. Sci. 574, 331 (2005).

V.N. Antonov, J.S. Palmer, P.S. Waggoner, A.S. Bhatti, and J.H. Weaver, "Nanoparticle Diffusion on Desorbing Solids: The Role of Elementary Excitations in Buffer-Layer-Assisted Growth," Phys. Rev. B 70, 045406 (2004).

J.H. Weaver and V.N. Antonov, "Synthesis and Patterning of Nanostructures of (Almost) Anything on Anything," Surface Science 55, 1 (2004). See also C&E News 82, 6 (May 3, 2004), Science (Editor's Choice) 304, 797 (2004), and Physics Today, pp. 22-23, June 2004.

V.N. Antonov and J.H. Weaver, "CO-induced Morphology Modification in Buffer-Layer-Assisted Growth of Pd Nanostructures," Surface Science 526, 97 (2003).

V.N. Antonov, J.S. Palmer, A.S. Bhatti, and J.H. Weaver, "Nanostructure Diffusion and Aggregation on Desorbing Rare-gas Solids: Slip on an Incommensurate Lattice," Phys. Rev. B 68, 205418 (2003).

(b) non peer reviewed

None

(c) papers presented at meetings but not published

J.H. Weaver "Buffer-Layer-Assisted Growth and the Formation of Nanostructures of (Almost) Anything on Anything," AVS Distinguished Lecture, AVS New Mexico Chapter, Albuquerque, May 2004.

J.H. Weaver, V.N. Antonov, J.S. Palmer, and A.S. Bhatti, "Nanoparticle Diffusion and Aggregation on Desorbing Rare Gas Solids: Slip on an Incommensurate Lattice," IVC-16/ICSS-12/NANO-8, Venice, June 2004.

J.H. Weaver, "Buffer-Layer-Assisted Growth and the Formation of Nanostructures of (Almost) Anything on Anything," International Conference on Surface and Interface Science, Tel Aviv, October 2004.

V.N. Antonov, J.S. Palmer, P.S. Waggoner, A.S. Bhatti, and J.H. Weaver, "Nanoparticle Diffusion on Desorbing Solids: The Role of Elementary Excitations in Buffer-Layer-Assisted Growth," Understanding Complex Systems Symposium, Urbana, May 2004. Antonov won "best poster of the conference."

V.N. Antonov, J.S. Palmer, P.S. Waggoner, A.S. Bhatti, and J.H. Weaver, "Nanoparticle Diffusion on Desorbing Solids: The Role of Elementary Excitations in Buffer-Layer-Assisted Growth," AVS Prairie Chapter, Urbana, June 2004.

K.S. Nakayama, T. Sugano, K. Ohmori, and J.H. Weaver, "Spectroscopy for Individual Atoms," Institute for Materials Research, Tohoku University, Sendai, August 2004.

K.S. Nakayama, T. Sugano, K. Ohmori, and J.H. Weaver, "STM and STS for Fingerprinting of Adatoms on Si(100)," Advanced Research Laboratory, Hitachi, Saitama, August 2004.

V.N. Antonov, J.S. Palmer, P.S. Waggoner, A.S. Bhatti, and J.H. Weaver, "Nanoparticle Diffusion on Desorbing Solids: The Role of Elementary Excitations in Buffer-Layer-Assisted Growth," AVS 51st International Symposium, Anaheim, November 2004.

J.S. Palmer, V.N. Antonov, A.S. Bhatti, P.S. Waggoner, P. Swaminathan, and J.H. Weaver, "Rare Gas Solid Grains and Grooves: The Influence of Film Structure on Buffer-layer-assisted Nanostructure Assembly," 65th Annual Physical Electronics Conference, Madison, June 2005.

J.S. Palmer, V.N. Antonov, A.S. Bhatti, P. Swaminathan, P.S. Waggoner, and J.H. Weaver, "The Effects of Buffer Structure on Buffer-Layer-Assisted Growth: Grain Boundaries, Grooves, and Pattern Transfer," Dynamics of Materials Revealed by Electron Microscopy, Urbana, June 2005.

V.N. Antonov, J.S. Palmer, A.S. Bhatti, and J.H. Weaver, "Buffer-Layer-Assisted Growth and the Formation of Nanostructures of (Almost) Anything on Anything," Dynamics of Materials Revealed by Electron Microscopy, Urbana, June 2005.

V.N. Antonov, J.S. Palmer, A.S. Bhatti, and J.H. Weaver, "Buffer Layer Assisted Growth and the Formation of Nanostructures of (Almost) Anything on Anything," 30th International Nathiagali Summer College on Physics and Contemporary Needs, Islamabad, July 2005.

J.S. Palmer, V.N. Antonov, A.S. Bhatti, P.S. Waggoner, P. Swaminathan, and J.H. Weaver, "Rare Gas Solid Grains and Grooves: The Influence of Film Structure on Buffer-layer-assisted Nanostructure Assembly," 30th International Nathiagali Summer College on Physics and Contemporary Needs, Islamabad, July 2005.

A.S. Bhatti, P. Swaminathan, V.N. Antonov, J.S. Palmer, and J.H. Weaver, "Photoluminescence from a-Ge Nanoparticles: Confinement Effects," 30th International Nathiagali Summer College on Physics and Contemporary Needs, Islamabad, July 2005.

(d) *Number of manuscripts*

1 in preparation

7. Participating Scientific Personnel

John H. Weaver, Principal Investigator & Professor

Honors and awards

D.B. Willett Professor of Engineering, University Illinois

AVS Distinguished Lecturer

Chair, AVS Board of Trustees

International Science Advisory Committee, National Center for Physics, Pakistan

US Councillor to the Int Union of Vacuum Science, Technique, and Application (IUVSTA)

ISI Highly Cited Researcher (#51 of top 1000 physicists with >12,500 citations)

Materials Science and Technology External Advisory Panel, Sandia National Laboratories

Long Range Planning Committee, AVS

Nomination Committee, AVS

Nomination Committee, American Physical Society

Advisor to Physics Today

Governing Board, American Institute of Physics

Editorial Boards include R&D Magazine, Surface Science, Central European Journal of Physics, Surface Science Spectra (associate editor)

In recognition of his research contributions and future promise, the University of Illinois awarded the PI with the Donald Bigger Willett Professorship. This award is recognition of work supported by the ARO. Investiture occurred on 3/31/04.

Research Personnel

Arshad Bhatti, Visiting Scientist

Koji Nakayama, Post Doctoral Research Associate

Vassil Antonov, Graduate Research Assistant

Jacob Palmer, Graduate Research Assistant – Will completed PhD in 2006

Phillip Waggoner, Undergraduate Research Assistant – Completed BS 8/05

Arshad S. Bhatti, a visiting professor from Pakistan, contributed to this program in 2002-2003 as a Fulbright Fellow. Upon his departure, we wrote a successful NSF-INT proposal that covers living expenses and limited supplies for Bhatti and his students when they are in residence at UIUC. It also covers travel for the US participants when they participate in nanoscience related workshops in Pakistan. Weaver and PhD student Palmer gave invited talks at the 30th International Nathiagali Summer College in July 2005. Weaver also gave a series of lectures in conjunction with high level meetings with Pakistan scientists and leaders in January 2005. Bhatti spent two months in 2004 at UIUC, contributing in a significant way to our BLAG work. His student, Aneeqa Bashir, spent three months at UIUC in 2005, learning the basics of BLAG so that she can set up a growth chamber at COMSATS-IIT in Islamabad as part of her PhD work.

In the low temperature scanning tunneling spectroscopy studies, we were assisted by Tomoko Sugano, a visitor from Japan who was sponsored by the Japan Patent Office to visit

a US laboratory for a year, and by Kenji Ohmori, a postdoc in Joe Greene's group at UIUC.

Philip Waggoner worked in WeaverLabs for three years and is coauthor of one paper that acknowledges ARO support. Philip was awarded a prestigious NDSEG fellowship.

Additional Demographic Information

- (a) number of faculty – 1
- (b) number of postdocs – 1
- (c) number of FTE postdocs – 0.5
- (d) number of grad students – 2
- (e) number of FTE grad students – 1
- (f) number of undergrads – 1
- (g) other staff – 0
- (h) number of BS awarded – 1 (Philip Waggoner)
- (i) number of MS degrees – 1 (Christina Haley)
- (j) Number of patents submitted – 0
- (k) Number of patents awarded – 0

8. Number of Inventions – None

9. Bibliography – None

10. Appendixes – None